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Oil-Polluted Water Treatment Using Nano Size Bagasse Optimized-Isotherm Study

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Abstract

The preliminary studies were conducted in order to evaluate the ability and behavior of sugarcane bagasse (generated as waste material from sugar mill) to remove oil by-products from aqueous. In this work adsorption experiments were carried out in a batch reactor to obtain adsorption isotherms of oil by-product on sugarcane bagasse. The capacity of sugarcane bagasse to adsorb oil by-product from aqueous solutions was evaluated at different pH, adsorbent dose and initial concentration. Equilibrium isotherms were analyzed by Langmuir isotherm equations. Compare the result and Langmuir isotherm shown that adsorption of oil by-product on a sugarcane bagasse is favorable. The concentration which was reviewed in this study was much closed to concentration in the industrial water disposal effluents and Langmuir isotherm did describe well the adsorption behavior obtained for these systems.

Keywords: Adsorbent, Equilibrium Isotherm, Nano, Oil by-Product, Sugarcane Bagasse

Introduction

Oil pollution has become one of the most serious global environmental issues during the last 30 years. It exists in different forms and is generated by various sources. The major sources of oil pollution in the ocean and other waterways include the runoff of oil and fuel from land-based sources, accidental spills from tankers, and oil drilling accidents (Fingas, 2001). So, one of the most challenging environmental problems today is removal of oil and other organic containments from industrial wastewater. Oil that exists in contaminated water can be classified as light hydrocarbon, heavy hydrocarbon, lubricant, fats (founded in plants or animal types) and cutting fluids (none emulsifies oils such as greases and emulsified oils such as water-soluble oil) (Wang et al., 2010). Oil is usually removed from wastewater prior to discharge to the environment to meet the maximum allowable limit of oil and grease in water as required by local enforcing agency (Mehrizad et al., 2012). Many technologies have been established for such removal, including chemical oxidation/reduction, biological treatment, coagulation/flocculation, adsorption, membrane separation, and ion exchange. Novel technologies are continuously being developed through the constant efforts of researchers (Wahi et al., 2013), Among this processes that employed to remove these pollutants, adsorption has drawn great attention because processes based on this concept are simple, highly efficient, and easy to operate therefore, adsorption processes are widely used especially processes which use low-cost adsorbing materials, such as biomass (Namasivayam et al., 2001; Amin, 2008; Jia et al., 2013). Various adsorbents have been developed for the removal of organic pollutants (e.g., dyes, pesticides, pharmaceuticals/drugs, and phenols) from water (Alexander et al., 2012). The highly hydrophobic characteristic of biomass combined with its high porosity; develop a capillary force towards the adsorption of oils. Vegetal tissues, with large surface area and big pores, tend to adsorb organic contaminants through physical and chemical mechanisms, in a similar way to charcoal. The importance of systematic utilization of bagasse or sugar cane cellulosic residues has been noted in the past decade. Environmental concerns have fueled this focus not only because of the quantity of bagasse produced annually but also because of the nature of the material. Table 1 presents a brief literature review of sugarcane bagasse uses as adsorbent. It is interesting to notice that most of references used modified sugarcane bagasse. Although it can be seen that modified bagasse is very efficient to adsorb a variety of compounds (Poliana et al., 2010; Almazan et al., 1998). In this study the Nano sized sugarcane bagasse was modified with acetic anhydride and was selected as a natural organic sorbent. The adsorption experiments were carried out in a Pyrex batch reactor at room temperature to obtain the adsorption isotherm Langmuir was used to correlate the experimental data.

Table 1. Literature references about use of sugarcane bagasse as an adsorbent.

Absorbent	Adsorbate	PH	Ads. capacity (mg/g)	Ref.
Treated sugarcane bagasse	Pb	5.00	227.7	(Swaminathan et al., 2005)
Mercerized sugarcane bagasse	Cu(II)Cd(II)Pb(II)	5.40 7.00 6.00	153.9 250.0 500.0	(Gurgel et al., 2008)
Mercerized sugarcane bagasse	Ca(II) Mg(II)	10.00 9.00	54.1 42.6	(Karnitz et al., 2009)
Modified sugarcane bagasse	Sulphate ions	10.00	38.0 400.0	(Mulinari et al., 2008)
Chemically modified sugarcane bagasse	Cu(II)Cd(II)Pb(II)	5.50 66.50 7.55	139.0 313.0 313.0	(Karnitz et al., 2007)
Modified sugarcane bagasse	Cr(VI)	3.00	103.0	(Wartelle et al., 2005)

Experimental

Preparation of the sorbent material

Raw sugarcane bagasse was obtained from Karun Agro-Industry factory. Sugarcanes bagasse were washed in distilled water for times and then dried in open air prior to preparation for adsorption experiment. This bagasse was crashed with the vegetable crusher to smaller size. The sorbent should to made in nanometer size so raw bagasse was crashed for 2hr in vegetable crusher and then passed through different sieves (mesh number 100 and 200) to achieve particle with micro size (particle are about 74-149 µm). Due to smaller sorbent size has higher sorption capacity in this work Nano sized sugarcane bagasse was used. For this purpose micro sized sugarcane bagasse that produced was milled for 4hr in a high energy ball mill to convert its structure to Nano size. Then Nano size sugarcane bagasse was washed in distilled water to remove the water-soluble particle and surface adhered particles and then dried in oven for 16hr at 80°C. After this stage, the physical and chemical characterization of the adsorbent was carried out. 15g of micro size sugarcane bagasse was well mixed with 300 ml acetic anhydride and 3g NBS (N-bromomsuccinimide), and were put in a 500ml Pyrex batch reactor that was equipped with a reflux condenser. This setup was put in oil bath at 100°C for 2.5hr. After reaction time this modified bagasse was separated and thoroughly washed with ethanol and acetone until removed the un-react acetic anhydride and acid by-product then was dried in a hot air oven at 60°C for 16hr.

Adsorption experiment

Samples of crude oil were collected from the National Iranian South Oil Company (NISOC). In this study sorption capacity of sorbent was determined according to test ASTM (American standard test method) F726-99 test to create a stable oil emulsion. Oil by-product was dispersed in water and the surfactant Tween 80 was used in proportion 0.5% volume percent. Then magnetic stirrer at speed of 1000 rpm was use for 24hr to mix it perfectly. In order to determine the sorption capacity and study a effect of different condition 100 ml of contaminated water with different concentrations (200, 600, 1000 ppm) was placed in flask and a certain amount of sorbent was added then the set was placed in incubator at the speed 150 rpm and for 3hr. at end of experiment sorbent was separated from aqueous by centrifugal filtration. To determine the concentration of oil by-product in aqueous, the water COD was determined before and after the adsorption.

Results and Discussion

Raw bagasse is a combination of cellulose, lignin, and other minor components. It is a material that absorbs hydrophilic and hydrophobic materials. The mechanism is partly because there are hydrophilic and hydrophobic sites of bagasse that can attract these materials, respectively. Cellulose molecules are more attracted to hydrophilic than to hydrophobic materials (Chiparus, 2004). To improve these properties of bagasse, Nano size bagasse was modified by acetylation reaction with acetic anhydride, using NBS (N-bromomsuccinimide) as a catalyst. While the role of NBS is not clear but it attributed to Br^+ (Diao et al., 2010). Figure 1 shows the mechanism of this reaction based on the study of acetylation of alcohols.

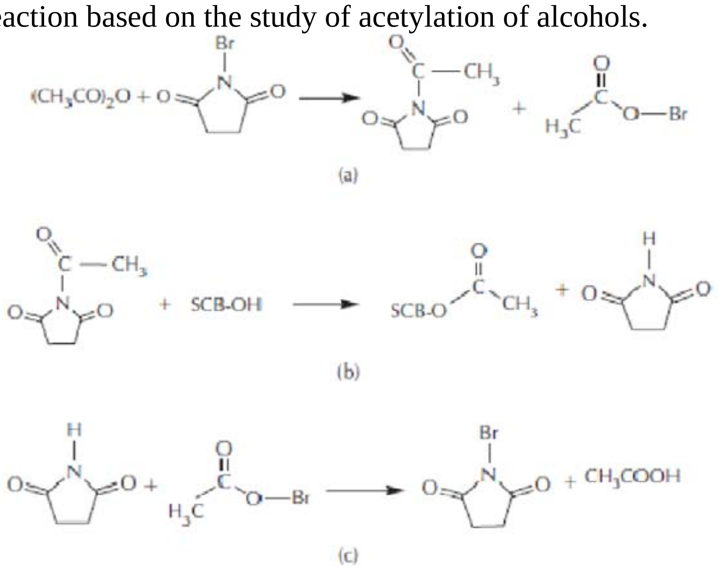

Figure 1. Mechanism of acetylation of raw bagasse using NBS as a catalyst (Diao et al., 2005).

Analysis of FTIR test

Sugarcane bagasse is a cellulose matrix, which has different binding sites, including carboxyl (–COOH) and hydroxyl (–OH) groups. Infrared spectroscopy is a useful tool to confirm the occurrence of graft copolymerization. As shown in Figure 2a and b the IR spectrum of the for raw sugarcane bagasse and sugarcane bagasse modified with acetic anhydride and NBS (N-bromomsuccinimide) showed strong bands at about 3400 cm^{-1} could be assigned to the stretching vibration of O–H (hydroxyl groups) and a medium signal, between 1500-1700 cm^{-1}, is due to the carboxylic groups, present in lignin and hemi-cellulose. When compare the FTIR of raw bagasse before and after the treatment see that peak in region, 3700-3400 cm^{-1} for O-H, was reduced also that indicate the hydroxyl group content in modified bagasse was reduced after treat, at 3446 cm^{-1}. Other major different between raw bagasse and modified bagasse was shown are occurrence of two important ester band at 1749, and 1244 cm^{-1}, which are attributed to adsorption by carbonyl bonds (C=O ester), and -C-O- stretching in ester (-C-O- in acetyl group), respectively.

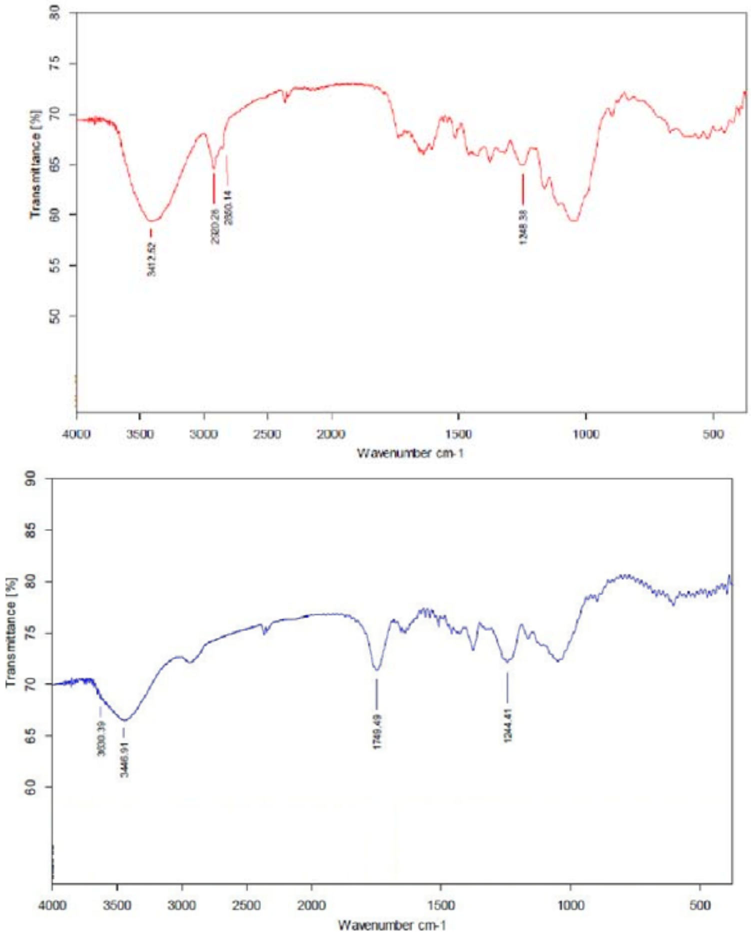

Figure 2. a(upper) and b(Lower) infrared spectrum of modified bagasse

Effect of initial oil-by product concentration

Oil initial concentration affects oil removal from wastewater as the oil initial concentration influences the oil adsorption kinetics (Ahmad et al., 2005). It seems that, at high oil concentration, oil occupies the sorbent surface thus saturation is reached much faster and high amount of unattached oil is left (Huan and Lim, 2006). But what we've seen is inconsistent with what would be expected. To study the effect of the initial concentration of oil by-product in the solutions, the experiment were carried out at a fixed modified micro size bagasse dose (6 g) and at different initial oil by-product concentrations (200, 600, 1000 ppm) other parameter such as retention time and temperatures and PH are fixed at 3 hr and 25 °C and 7 respectively. Figure 3 shown this result.

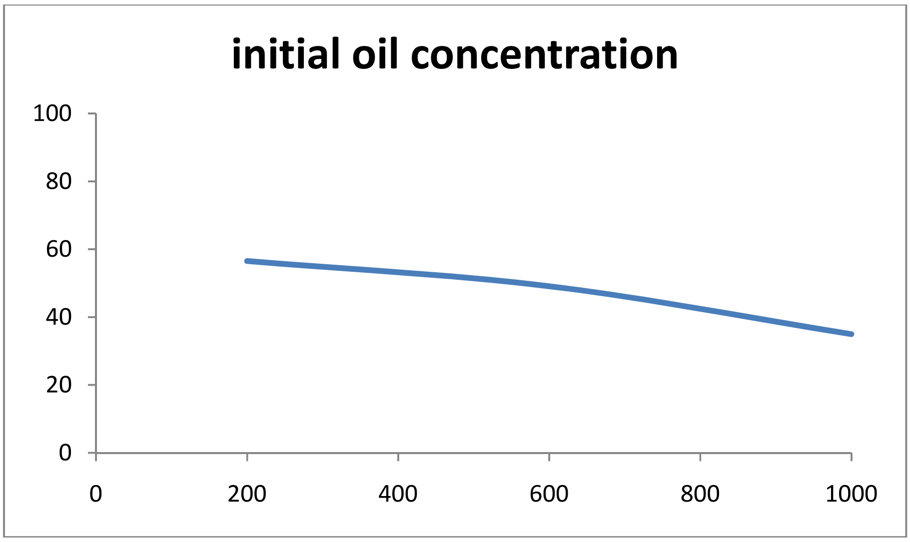

Figure 3. Removal efficiency Vs Initial oil concentration (ppm)

Effect of Sorbent dosage on oil by-product adsorption

With increase the sorbent dosage, oil removal efficiency will increased. The phenomenon is associated with an increase in available binding sites for adsorption in higher sorbent dosage (Ahmad et al., 2005). However, sorption capacity decreases with an increase in sorbent dosage, mainly due to the increase of unsaturated oil binding sites (Ibrahim et al., 2010). In addition, saturation effect also causes a decrease in oil removal efficiency when maximum sorption capacity has been reached (Rajakovic-Ognjanovic et al., 2008). The experiments are done for oil by-product concentration (600 ppm) and different sorbent dosage (2, 6, 10 g). Figure 4 shows the effect of sorbent dosage in removal efficiency.

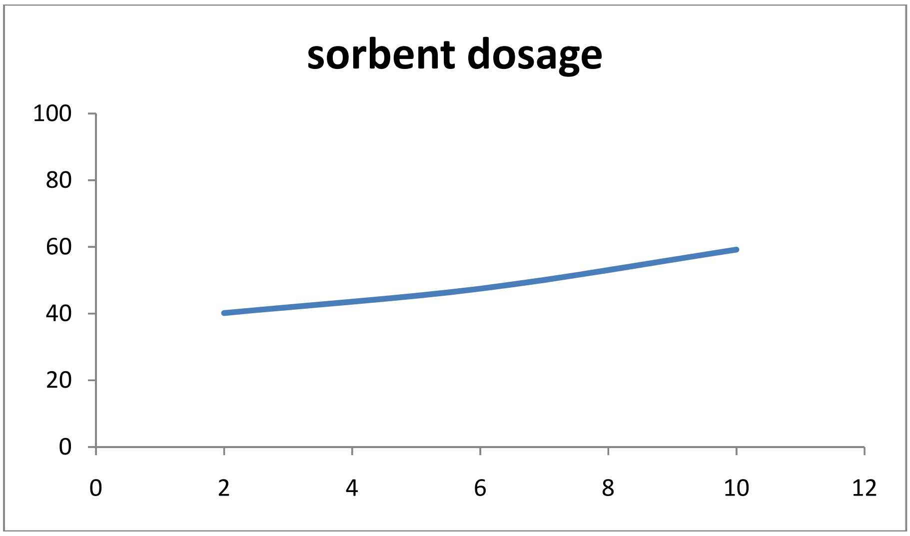

Figure 4. Removal efficiency Vs Sorbent dosage (g)

Correlation of experimental results

The result that obtained from experiment was used in the thermodynamic modeling of the adsorption process. Langmuir isotherm is the models which tested because this is the model most often mentioned in the literature to describe adsorption processes in liquid phase.

$$q_{eq} = \frac{q_{max} b C_{eq}}{1 + b C_{eq}} \qquad \textit{Langmuir eq} \text{ (Langmuir, 1918)}$$

In above equation C_{eq} is the concentration of adsorbate in equilibrium (mL/mL) and q_{eq} is the adsorbed amount per gram of adsorbent (mL/g) in the equilibrium. In the Langmuir isotherm, q_{max} characterizes the practical limiting adsorption capacity when the surface is fully covered by oil by-product and b is the Henry's constant, parameter related to the force between adsorbate and adsorbent and represents the bond energy related to the adsorption phenomenon between oil by-product and sorbent materials. A linearized plot of C_{eq}/q_{eq} against C_{eq} is obtained from the Langmuir model and is shown in Fig 3.3. q_{max} and b were computed from the slopes and intercepts of straight lines obtained from linear regression analysis of the experimental data (Fig 5). The high coefficients of determination obtained by fitting experimental data with Langmuir model indicate that the adsorption phenomenon of oil by-product can be described by this model. The results for oil by-product adsorption on sugarcane bagasse using Langmuir model are presented in Table 2. The value of R given in Tables 2 and 3 shows that favorable adsorption of oil on sugarcane bagasse takes place. Therefore, the prepared sugarcane bagasse is favorable adsorbents. The mechanism of adsorption may involve three steps: (1) diffusion of oil by-product particle residue to the external surface of adsorbent; (2) diffusion into the pores of adsorbent; (3) adsorption of the residue on the internal surface of adsorbent. The first part of adsorption could be affected by the initial concentration. The final step of the adsorption is considered as a rate-determining step and as a relatively rapid process (Sokker et al., 2011).

Table 2. Langmuir isotherm constant.

Material	Q_{MAX}	b	R^2
Oil by-product	12.25	2.89	0.9981

Table 3. The parameter R indicates the shape of isotherm as follows.

Value of R	Type of Isotherm
R > 1	Unfavorable
R = 1	Linear
0< R < 1	Favorable
R = 0	Irreversible

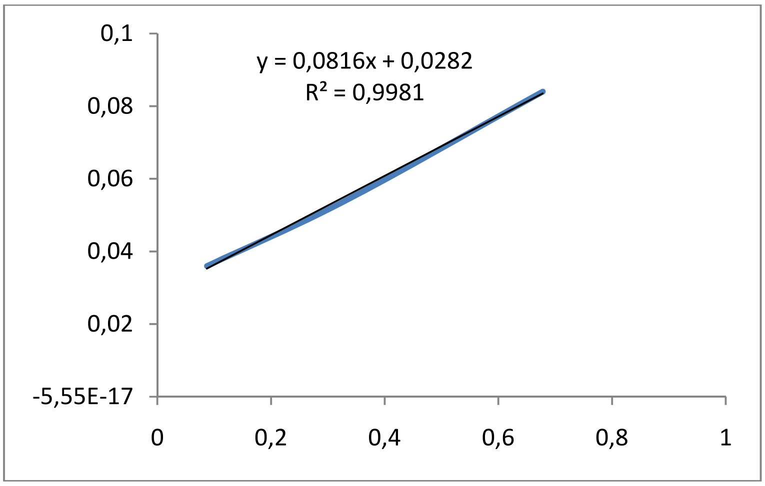

Figure 5. Linearized plot of C_{eq}/q_{eq} VS C_{eq}

Adsorption isotherms

The adsorption isotherms of oil by-product on sugarcane bagasse at room temperature are presented in Figure 6 Experimental data are presented along with the results of the correlation obtained through the isotherms of Langmuir.

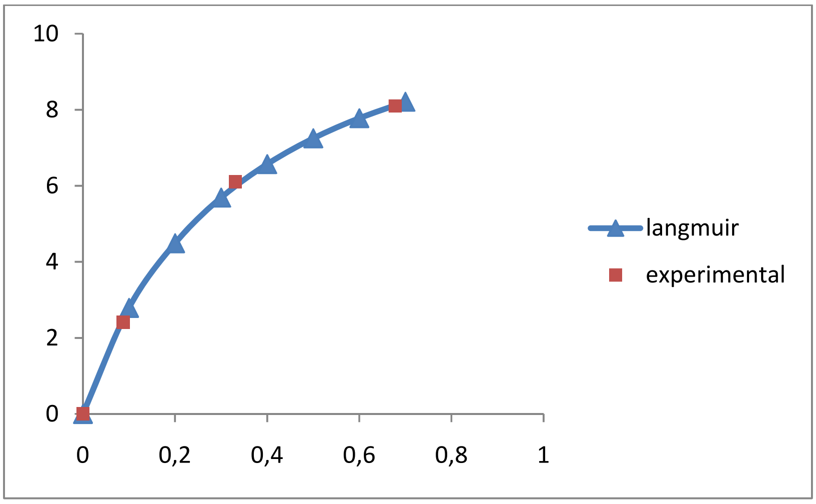

Figure 6. Adsorption isotherm of oil by-product on sugarcane bagasse at room temperature (experimental adsorbed amount in the equilibrium q_{eq} (ml/g) Vs concentration of adsorbate in equilibrium C_e (ml/mL)).

The shape of isotherm which shown in this diagram is like of a common action in physic adsorption with good adsorption force between adsorbate and adsorbent. The first points are characteristic of a concave favorable isotherm such as a Langmuir isotherm. This kind of shape is named class L (Giles et al., 1960). According to Giles et al., in this class of adsorption, large amounts can be adsorbed at low concentrations of solute which observed by Rather high percentage of adsorbed oil by-product on sugarcane bagasse in this region (Giles et al., 1960). In this isotherm class, five sub-groups are presented, too which named 1,2,3,4 and mx (Ahmad et al., 2005). So the isotherm shapes of this study it fitting with class L sub-group 2. L2 curve occurs in probably the majority of cases of adsorption from dilute solution and few cases of the other types appear to have been previously recorded (Ahmad et al., 2005). In this class of Langmuir isotherm the rate at which molecules bombard the surface is assumed to be directly proportional to the pressure (or concentration, of a solution) that in this study it's depending to concentration of oil by product in aqueous. A further assumption, necessary in applying the Langmuir concept to solution adsorption, which we make in common with earlier authors, is that in adsorption from dilute solution the action of the solvent molecules is solely to reduce the energy of the surface, by competition with the solute (Ahmad et al., 2005). This assumption is explains the behavior of isotherm shape in this study perfectly. All the isotherms fitted well the experimental data of oil by-product adsorption and no sensible errors observed between the experimental and correlated data because the concentration of oil by-product was low and adsorption done in one layer and Langmuir isotherm explains as well as monolayer adsorption.

Conclusion

From result of this study can be concluded that the shape of isotherm of this study was classified in L2 (class L and sub-group 2) indeed the L2 curve occurs in probably the majority of cases of adsorption (Giles et al., 2005). The Langmuir model was explained this study relatively and without sensible error because the concentration of aqueous was law. Fortunately, this range of concentration is the region with the more usual concentration in the industrial water disposal effluents. Also data which obtained from experiment indicate that the use of sugarcane bagasse as an adsorbent of non-polar substances such as oily material is very favorable.

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